

Size control of Charge-Orbital Order in Half-Doped Manganite, $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$

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Motivated by recent experimental results, we study the effect of size reduction on half-doped manganite, $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, using the combination of density functional theory (DFT) and dynamical mean field theory (DMFT). We find that upon size reduction, the charge-ordered antiferromagnetic phase, observed in bulk, to be destabilized, giving rise to the stability of a ferromagnetic metallic state. Our theoretical results, carried out on defect-free nanocluster in isolation, establish the structural changes that follow upon size reduction to be responsible for this. Our study further points out the effect of size reduction to be distinctively different from application of hydrostatic pressure. Interestingly, our DFT+DMFT study, additionally, reports the correlation-driven stability of charge-orbitally ordered state in bulk $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, even in absence of long range magnetic order.

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Size controls the physical properties of materials and can hence be employed to make materials functional. For strongly correlated materials, theoretical modelling of such phenomena is rare. Here, we pursue such a study taking the case of half-doped manganites. The charge and orbitally ordered state observed in half-doped manganites is one among the rich variety of fascinating phenomena exhibited by perovskite manganites $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ (R= rare-earth element; A= alkali-earth element).¹ The charge-ordered (CO) state is associated with a real space ordering of $\text{Mn}^{3+}/\text{Mn}^{4+}$ species in a 1:1 pattern. It is accompanied by orbital ordering (OO) and a structural change from orthorhombic to monoclinic symmetry which gives rise to an insulating ground state.²⁻⁶ The insulating CO state has been reported to be destabilized to a ferromagnetic (FM) metallic phase by various means that include a magnetic field,⁷ doping, biaxial strain, pressure,⁸ and electric field.⁹ Very recently, it has been shown in a few experimental studies¹⁰⁻¹² that the destabilization of the CO state can be achieved even through size reduction. This interesting phenomenon adds another dimension, namely size, to the problem. Size control is attractive from a technology point of view, which is achievable chemically in a low-cost way. The route through size control also opens up the possibility of exploring the tunability of the CO-OO state and the associated metal-insulator transition.

In this letter, we study the effect of size reduction on the CO-OO state of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (LCMO) by using a combination of First-principles DFT and DMFT. For the DFT calculations, we used a combination of two methods: (a) plane wave-based pseudopotentials,¹³ and (b) muffin-tin orbital (MTO) based on linear muffin-tin orbital¹⁴ (LMTO) and N-th order MTO (NMTO).¹⁵ For (a) we used projected augmented wave pseudopotentials with an energy cutoff of 450 eV. We used a spin polarized generalized gradient approximation (GGA).¹⁶ From a self-consistent DFT calculation, a low-energy Mn- e_g only model Hamiltonian was constructed using NMTO-

downfolding technique.¹⁵ The corresponding Hubbard Hamiltonian defined in the downfolded NMTO basis was solved using DMFT, in the same spirit as previously carried out in in Ref. 17 in the context of pure LaMnO_3 . The low-energy model Hamiltonian consists of two e_g orbitals per Mn ion with intra-orbital Coulomb interaction $U = 5\text{ eV}$ and Hund's exchange $J = 0.75\text{ eV}$ which are coupled by $\mathcal{J} = 1.35\text{ eV}$ to a (classical) spin representing the half-filled and immobile t_{2g} electrons. The DMFT equations were solved by Hirsch-Fye quantum Monte Carlo simulations¹⁸, and, because of the CO ordering, it was necessary to explicitly consider a site-dependent double counting correction.¹⁹

Bulk LCMO shows a CO transition at $T_{co} = 155\text{ K}$. Below 155 K, the crystal structure is of monoclinic symmetry ($P2_1/m$) and an antiferromagnetic (AFM) order sets in.²⁰ The magnetic structure, the so called "CE" order, consists of zig-zag FM chains that are coupled antiferromagnetically in the crystallographic ac plane. The ac planes are stacked antiferromagnetically along the crystallographic b -direction. A noteworthy feature of the crystal structure is that while the Jahn-Teller (JT) distortion is sizable for the bridge-site Mn atoms (Mn1) with two long bonds along the FM chain and four short bonds, the corner-site Mn atoms (Mn2) on the zigzag chains have negligible distortion with nearly similar Mn-O bondlengths. Average Mn2-O distance is smaller than that of Mn1-O.² Our DFT calculations carried out on the experimentally measured structure,² henceforth, referred as S_{ex} , showed the CE insulating phase to be stable by 18 meV/f.u. over the FM metallic solution. The calculated electronic structure in terms of density of states and magnetic moments are found to be in good agreement with those reported previously in literature.²¹

In order to study the problem of nanoscale LCMO we first created a large supercell in the monoclinic structure, from which a cluster of diameter 2-3 nm having approximate spherical shape was cut out (cf Fig. 1, left panel), in which we carried out a full structural optimization.

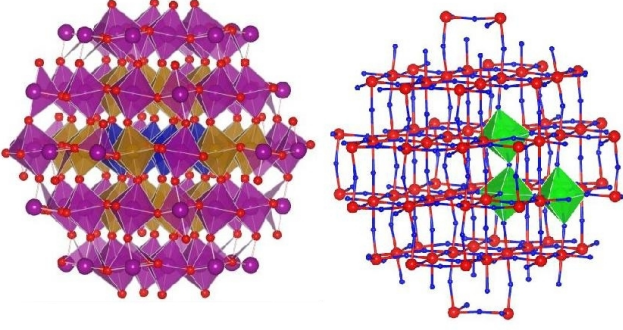


FIG. 1: (Color online) Left Panel: Constructed nanocluster of LCMO. In magenta (dark grey), brown (light grey) and blue (deep, dark grey) we show the MnO_6 octahedra belonging to the outer most surface layer, next to the surface and the core region. Right Panel: The structural unit, highlighted in green (grey), chosen out of S_{nano} , used for building up of S_{model} . The big and small spheres in the unshaded region represent Mn and O atoms respectively.

Following this procedure, the 2 nm cluster contains a total of 370 atoms and the 3 nm cluster contains a total of 700 atoms, pushing it to a limit of our DFT structural optimization. In the construction of the clusters, care has been taken to maintain the stoichiometry as closely as possible. For the cluster calculation, a simple cubic supercell was used with periodic boundary conditions, where two neighboring clusters were kept separated by 10 Å, which essentially makes the interaction between cluster images negligible. The positions of the atoms were relaxed towards equilibrium, using the conjugate gradient technique until the Hellmann-Feynman forces became less than 0.001 eV/Å.

The considered DFT cluster sizes are smaller than the experimental realizations¹⁰ of sizes 15 nm. Hence only the inner region of the above constructed clusters of 2-3 nm size, is expected to mimic the prototypical behavior of the experimentally studied clusters. In order to understand the consequences of the size-controlled structural changes for such relatively larger clusters, we hence constructed a model bulk system, which we refer as S_{model} . It is built out of the structural units belonging to the innermost core and the next to the core layer of the optimized LCMO in the nanoscale geometry, (referred as S_{nano}), as shown in the right panel of Fig. 1, and subsequently imposing the symmetry considerations. The detailed procedure of construction of model system is explained in the supplementary information (SI). Construction of S_{model} leads to consideration of the local oxygen environments around Mn atoms as well as the tilt and rotation connecting two MnO_6 octahedra, same as that in core region of S_{nano} . The lattice parameters and the Mn-O bond lengths of S_{model} are compared to the bulk structure in Table I. The detailed structural information can be obtained in SI. Note, for the bulk, we have considered the theoretically optimized structure, re-

	S_{bulk}				S_{model}			
Lattice	$a = 5.47, b = 7.58$				$a = 5.28, b = 7.49$			
param.	$c = 5.48$				$c = 5.39$			
Mn1-O:	2.18	1.93	1.94	2.02	1.97	1.92	1.91	1.93
Mn2-O:	1.92	1.92	1.94	1.93	1.92	1.88	1.92	1.91

TABLE I: Lattice parameters, and Mn-O bondlengths (in Å) of S_{model} in comparison to S_{bulk} . The entries for Mn-O bondlength from left to right correspond to that along the FM chain, between the FM chains, along b -direction and the average. Mn1 atoms are of nominal valence 3+ and Mn2 of 4+.²²

ferred as S_{bulk} , in order to compare with parameters of S_{model} in the same footing. We find that the lattice parameters of S_{model} show substantial reduction compared to those of the bulk system. The change in a parameter appears to be the largest with a change of about 0.20 Å, with moderate changes in b and c parameters, of 0.09 Å's. Qualitatively, this trend of reduction in lattice parameters and also the nature of reduction agrees very well with the crystal structure data extracted from X-ray diffraction of nanoclusters of LCMO of 15 nm size [cf. Fig 4 in Ref.10(a)]. We note that the reduction in lattice parameters in the model structure gave rise to about 6% reduction in the volume compared to that of the bulk system; the first experiments¹⁰ report a 2% reduction. The 6% reduction was obtained for S_{model} constructed out of S_{nano} of 3 nm, while a similar procedure for S_{nano} of 2 nm, gave rise to larger volume reduction ($\approx 8\%$). This indicates the volume reduction to increase upon decreasing cluster size, justifying the difference between the obtained volume reduction on 2-3 nm cluster and experimentally observed volume reduction on 15 nm cluster. One of the important structural quantities is the orthorhombic strain: $\text{OS}_{\parallel} = 2 \frac{(c-a)}{(c+a)}$ gives the strain in the ac plane, while $\text{OS}_{\perp} = 2 \frac{(a+c-\sqrt{2}b)}{(a+c+\sqrt{2}b)}$ is that along the b -axis. For S_{bulk} , the orthorhombic strain is highly anisotropic with a negligible value of OS_{\parallel} (≈ 0.002) and a high value of OS_{\perp} (≈ 0.021). For S_{model} , we find instead the orthorhombic strains to be comparable ($\text{OS}_{\parallel} \approx 0.02$ and $\text{OS}_{\perp} \approx 0.01$). This trend is also in very good agreement with experimental results.¹⁰ It confirms that our constructed model structure captures the essential structural changes in the nanoscale surprisingly well. This proves that the role of surface beyond what is already taken into account in construction of model structure, is small.

Next, we calculated the electronic structure for S_{model} and compared it with that of S_{bulk} . For understanding the results, let us note that the difference between the average Mn1-O and Mn2-O bondlengths is smaller in S_{model} than in S_{bulk} . This leads to the expectation that the charge disproportionation (CD) between Mn1 and Mn2 sites to decrease in S_{model} . Furthermore, we note that for S_{bulk} , the difference between the longest

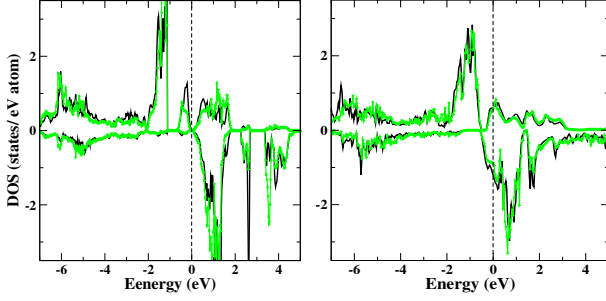


FIG. 2: (Color online) DFT DOS, projected onto Mn1- d (black solid line) and Mn2- d (green/light grey line) states calculated for the CE phase of S_{bulk} (left panel) and the FM phase of S_{model} (right panel). The zero of energy is set at E_F .

and the shortest Mn-O bondlengths is large for Mn1 and tiny for Mn2. This gives rise to the crystal field splitting (Δ) between the two Mn- e_g states, Mn- $3z^2 - r^2$ and Mn- $x^2 - y^2$, as large as 0.63 eV for Mn1 sites and less than 0.02 eV for the Mn2 sites. In contrast for S_{model} , the bond length differences are much more similar for both types of Mn sites. This is reflected in similar Δ 's for the nano model, i.e., 0.15 eV for Mn1 sites and 0.10 eV for Mn2 sites. Together these two effects weaken CO as well as OO in S_{model} . This ordering is important to stabilize the AFM structure found for the bulk. With charge and orbital ordering weakened, we find instead FM to be stable by 20 meV in S_{model} . This result is in accordance with the experimental observations.^{10,11} The microscopic origin of the size controlled transition from AFM to FM, therefore, can be traced back to the size-induced structural changes.

Fig. 2 shows the density of states (DOS) of S_{bulk} with AFM ordering of Mn spins, in comparison to that of S_{model} with FM ordering. Considering the DOS for S_{bulk} , the crystal field splitting between Mn- $3z^2 - r^2$ and Mn- $x^2 - y^2$ is clearly seen. In the majority spin channel, Mn- $3z^2 - r^2$ states at Mn1 site are more occupied than the Mn- $3z^2 - r^2$ states at Mn2 site, giving rise to CD between Mn1 and Mn2. We also find OO at Mn1 sites with a preferential occupation of Mn- $3z^2 - r^2$ over Mn- $x^2 - y^2$. The CO, although incomplete, together with the AFM spin ordering gives rise to an insulating solution with a small but finite gap at E_F already at the DFT level. Considering the DOS of S_{model} , we find that the splitting between Mn- $3z^2 - r^2$ and Mn- $x^2 - y^2$ is less pronounced and the Mn1- d and Mn2- d states to be similar. The reduced Δ together with the increased bandwidth, compared to the bulk structure, drives S_{model} to metallicity with a finite density of states at Fermi energy (E_F). The increased bandwidth is caused by the reduction in volume as well as by the FM ordering which allows hopping processes within a double exchange model.²³

In order to take into account the influence of the missing electronic correlation in GGA, we did paramagnetic DMFT calculations for S_{bulk} and S_{model} structures, con-

	Bulk		Nano-model	
Mn1(1)	0.87 (0.50)	0.01 (0.11)	0.52 (0.31)	0.09 (0.20)
Mn1(2)	0.85 (0.47)	0.01 (0.12)	0.72 (0.38)	0.04 (0.19)
Mn2	0.04 (0.15)	0.09 (0.25)	0.16(0.21)	0.16 (0.25)

TABLE II: Orbital occupancies for Mn- $3z^2 - r^2$ (first entry) and $x^2 - y^2$ (second entry) states calculated within DFT+DMFT for different inequivalent classes of Mn atoms in the unit cell for S_{bulk} and S_{model} . In brackets we give the corresponding occupancies for the one particle, low-energy DFT Hamiltonian.

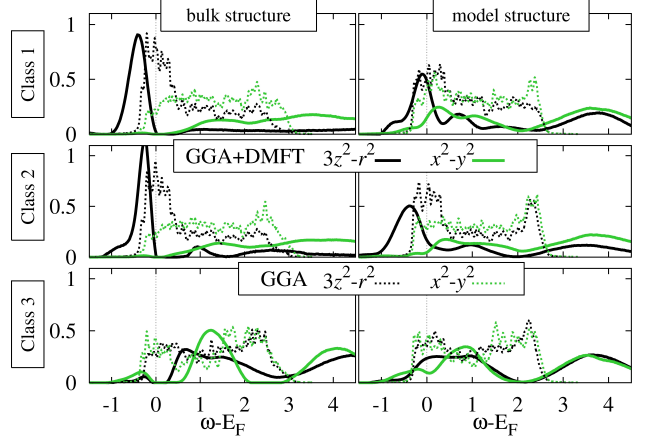


FIG. 3: (Color online) DFT+DMFT spectral densities for e_g states of three inequivalent classes of Mn (solid lines), corresponding to S_{bulk} and S_{model} . The dashed lines represent the corresponding DFT DOS. The lines colored as black and green (light grey) correspond to $3z^2 - r^2$ and $x^2 - y^2$ states, respectively.

sidering the low-energy Mn- e_g only Hamiltonian derived out of DFT. Table II lists the the orbital occupations of the three types of inequivalent Mn sites. For S_{bulk} , already in the DFT (in brackets) the two inequivalent Mn1 (“Mn³⁺-like”) sites (Mn1(1) and Mn1(2)) are more occupied than the Mn2 (“Mn⁴⁺-like”) sites.²⁴ Besides the CD, there is, as mentioned above, a DFT orbital order. Electronic correlations enhance both kinds of ordering dramatically, making CO and OO nearly complete. *This, establishes the correlation driven stability of CO and OO with almost complete CD in a paramagnetic phase.* The almost complete CD and enhanced orbital polarization (OP) at the Mn1 sites results in a gap at the chemical potential in the DFT+DMFT spectral function for the bulk structure, as shown in the left panel of Fig. 3, even without spin ordering. Note the opening of charge gap is stabilized by long-range Coulomb interactions which, within DMFT, reduce to their Hartree contribution. This effect is taken into account in our DFT+DMFT calculation on the GGA level. Compared to the DFT spectra, spectral weight is transferred to high frequencies in the form of Hubbard bands, opening a gap at the chemical potential. For the DFT calculation on the other hand,

the charge disproportionation is incomplete, and the insulating solution is obtained only by assuming the AFM spin ordering. Turning to S_{model} , the DFT occupancies show Mn^{3+} -like and Mn^{4+} -like sites to be similar with only a weak CD. The inclusion of correlation effect through DMFT enhances CD to some extent following the trend seen for S_{bulk} . However, CD remains incomplete with an average occupation of Mn^{3+} -like and Mn^{4+} -like sites of 0.6-0.7 and 0.3 respectively, in comparison to 0.9 and 0.1 respectively, obtained for S_{bulk} . *This conclusively establishes that size reduction leads to weakening of charge disproportionation.* This in turn leads to metallic DFT+DMFT solution for S_{model} with finite weight at the chemical potential, as shown in right panel of Fig.3. Note, although S_{nano} does not maintain the strict stoichiometry, the constructed S_{model} is strictly stoichiometric, pointing the fact that destabilization of CO is driven by the structural changes due to size confinement, rather than due to deviation from half-doping.

As one of the major structural changes upon size reduction is the volume compression, it is worthwhile to compare the structural and electronic changes induced by size reduction to those occurring under hydrostatic pressure. To this end, we carried out calculations of LCMO, with uniformly reduced lattice parameters with 6% reduced volume, the atomic positions being optimized in DFT, referred as structure S_{press} . The details of the optimized structure is given in SI. Following the self-consistent DFT calculations on S_{press} , the $Mn-e_g$ only low-energy Hamiltonian was constructed and the corresponding Hubbard Hamiltonian was solved using DMFT. Compared to S_{model} , first of all, we find that at the DFT level, CD and OP is much weaker, even though the volume is the same. With this less polarized starting point, all Mn sites are filled with ≈ 0.5 electrons. In this situation, electronic correlations are less relevant. The DMFT orbital and site occupations remain very similar to the DFT values with 0.4 - 0.6 electrons/site, and the system is far away from a metal-insulator transition (MIT). This leads us to conclude that the nanoscopic system is much closer to a MIT than bulk $La_{0.5}Ca_{0.5}MnO_3$ under hydrostatic pressure.²⁵ The size reduction and application of

hydrostatic pressure, therefore, should be considered as two very different routes.

In conclusion, using DFT calculations combined with DMFT, we have studied the effect of size reduction on charge-orbital order in half-doped LCMO manganites. Our study indicates that the size reduction leads to substantial reduction in volume as well as a change in the nature of the orthorhombic strain. The structural changes under size reduction lead to a weakening of both charge and orbital ordering, making the ferromagnetic metallic state energetically favorable compared to the “CE” type antiferromagnetic insulating state, which is the ground state of the bulk structure. While such effect has been observed, the experimental situation is faced with difficulties, like possible presence of impure phases, the grain boundaries, non-stoichiometry. Our theoretical calculations were carried out considering nanocluster in isolation, and therefore, devoid of such complications. Through construction of model structure, the issue of non-stoichiometry was avoided. Furthermore, the effect of size reduction turned out to be very different from that of pure hydrostatic pressure. We predict the nanoscopic system to be close to the MIT in comparison to the system under hydrostatic pressure with the same amount of volume reduction. Increasing the size of the nanocluster, one would expect to drive the system closer and closer to MIT. It would therefore be possible to tune the LCMO system to the verge of MIT, and thereby, achieve a large magnetoresistive response under small magnetic fields. Finally, while we carried out our investigation on LCMO, the destabilization has been predicted for $Pr_{0.5}Ca_{0.5}MnO_3$ too,²⁶ hinting to observed effect to be a more general one. This will be taken up in a later study.

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- ¹ Y. Tokura, Colossal Magnetoresistive Oxides (Gordon & Breach Science Publishers, New York, 2000).
 - ² G. Radaelli *et al.*, Phys. Rev. B **55**, 3015 (1997).
 - ³ M. Tokunaga *et al.*, Phys. Rev. B **57**, R9377, (1998).
 - ⁴ M. M. Savosta *et al.*, Phys. Rev. B, **65**, 224418, (2002).
 - ⁵ J. P. Joshi *et al.*, Phys. Rev. B **65**, 024410, (2001).
 - ⁶ J. P. Joshi *et al.*, J. Mag. Mag. Mat, **279**, 91, (2004).
 - ⁷ H. Kuwahara *et al.*, Science, **270**, 961 (1995).
 - ⁸ D. P. Kozlenko *et al.*, J. Phys. Cond. Mat., **16**, 5883 (2004).
 - ⁹ A. Asamitsu *et al.*, Nature (London), **388**, 50 (1997).
 - ¹⁰ T. Sarkar *et al.*, Phys. Rev. B **77**, 235112 (2008); T. Sarkar *et al.*, Appl. Phys. Lett **92**, 123104 (2008).
 - ¹¹ S. S. Rao *et al.* App. Phys. Lett, **87**, 182503 (2005).
 - ¹² T. Sarkar *et al.*, J. App. Phys. **101** 124307 (2007).
 - ¹³ G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
 - ¹⁴ O. K. Andersen, Phys. Rev. B, **12** 3060 (1975).
 - ¹⁵ O. K. Andersen and T. Saha-Dasgupta, Phys. Rev. B **62**, R16219 (2000).
 - ¹⁶ J. P. Perdew *et al.*, Phys. Rev. Lett. **77**, 3865 (1996).
 - ¹⁷ A. Yamasaki *et al.*, Phys. Rev. Lett. **96** 166401 (2006); Y.-F. Yang and K. Held, Phys. Rev. B **76** 212401 (2007); **82** 195109 (2010).
 - ¹⁸ J. E. Hirsch and R. M. Fye, Phys. Rev. Lett. **56** 2521 (1986).
 - ¹⁹ V. I. Anisimov, J. Zaanen and O. K. Andersen, Phys. Rev.

- B **44** 943 (1991).
- ²⁰ E. O. Wollan and W. C. Köhler, Phys. Rev. **100**, 545 (1955).
- ²¹ P. K. de Boer *et al.*, Solid State Commun. **102**, 621 (1997).
- ²² There are three inequivalent classes of Mn atoms in the unit cell, the first two are of nominal valence 3+ and the last one is of 4+. The structural parameters corresponding to only the first Mn³⁺ is shown. Also, for Mn⁴⁺-type three bondlengths are shown, taking the average of the pairs in the mentioned directions. For details see Table 2 of SI.
- ²³ P. W. Anderson and H. Hasegawa, Phys. Rev. **100** 675 (1955); P.-G. DeGennes, Phys. Rev. **118** 141 (1960).
- ²⁴ Calculation of CD in Pr_{0.5}Ca_{0.5}MnO₃ by Anisimov et al. [Phys. Rev. B **55** 15494 (1997)] showed negligible CD. The CD obtained in the present case, presumably is driven by the significant JT effect at M1 site.
- ²⁵ Although compression of volume and Mn-O bonds happen both in nanoscale and on application of pressure, the larger OS_{||}, in case of nanoscale compared to that under pressure makes the Mn-e_g bandwidth smaller for the former, through reduction in Mn-O-Mn bond angle.
- ²⁶ T. Sarkar *et al.*, J. App. Phys, **101**, 124307 (2007).